

424 Rec'd PCT/PTO

05 SEP 2001

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(REV. 11-2000)

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371

Mo-6617/STA-155

U.S. APPLICATION NO. (If known, see 37 CFR 1.5)

09/914984

To Be Assigned

INTERNATIONAL APPLICATION NO.

INTERNATIONAL FILING DATE

PRIORITY DATE CLAIMED

PCT/EP00/01667

28 February 2000 (28.02.00)

10 March 1999 (10.03.99)

TITLE OF INVENTION NICKEL HYDROXIDE COATED WITH COBALTOUS HYDROXIDE

APPLICANT(S) FOR DO/EO/US STOLLER, Viktor; ERB, Michael; OLBRICH, Armin and MEESE-MARKTSCHKE, Juliane

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND or SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☐ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below.
4. ☒ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
 - a. ☒ is attached hereto (required only if not communicated by the International Bureau).
 - b. ☐ has been communicated by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
 - a. ☒ is attached hereto.
 - b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
7. ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
 - a. ☐ are attached hereto (required only if not communicated by the International Bureau).
 - b. ☐ have been communicated by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☐ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371 (c)(3)).
9. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11 to 20 below concern document(s) or information included:

11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A **FIRST** preliminary amendment.
14. ☐ A **SECOND or SUBSEQUENT** preliminary amendment.
15. ☐ A substitute specification.
16. ☐ A change of power of attorney and/or address letter.
17. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
18. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
19. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
20. ☒ Other items or information:

Abstract

U.S. APPLICATION NO. (if known, see 37 CFR 1.53)
To Be Assigned **09/914984**INTERNATIONAL APPLICATION NO.
PCT/EP00/01667ATTORNEY'S DOCKET NUMBER
Mo-6617/STA-15521. ☒ The following fees are submitted:**BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)):**

Neither international preliminary examination fee (37 CFR 1.482)

nor international search fee (37 CFR 1.445(a) (2)) paid to USPTO

and International Search Report not prepared by the EPO or JPO \$1000.00

International preliminary examination fee (37 CFR 1.482) not paid to

USPTO but International Search Report prepared by the EPO or JPO \$860.00

International preliminary examination fee (37 CFR 1.482) not paid to USPTO

but international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$710.00

International preliminary examination fee (37 CFR 1.482) paid to USPTO

but all claims did not satisfy provisions of PCT Article 33(1)-(4) \$690.00

International preliminary examination fee (37 CFR 1.482) paid to USPTO

and all claims satisfied provisions of PCT Article 33(1)-(4) \$100.00

ENTER APPROPRIATE BASIC FEE AMOUNT =**CALCULATIONS PTO USE ONLY**

\$ 860.00

Surcharge of \$130.00 for furnishing the oath or declaration later than ☐ 20 ☐ 30
months from the earliest claimed priority date (37 CFR 1.492(e)).

\$ 0.00

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	\$
Total claims	22 -20 =	2	x \$18.00	\$ 36.00
Independent claims	4 -3 =	1	x \$80.00	\$ 80.00
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ \$270.00	\$ 0.00

TOTAL OF ABOVE CALCULATIONS =

\$ 976.00

☐ Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above
are reduced by 1/2.

\$ 0.00

SUBTOTAL =

\$ 976.00

Processing fee of \$130.00 for furnishing the English translation later than ☐ 20 ☐ 30
months from the earliest claimed priority date (37 CFR 1.492(f)).

\$ 0.00

TOTAL NATIONAL FEE =

\$ 976.00

Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be
accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property +

\$ 0.00

TOTAL FEES ENCLOSED =

\$ 976.00

Amount to be
refunded: \$

charged: \$

- a. ☐ A check in the amount of \$ _____ to cover the above fees is enclosed.
- b. ☒ Please charge my Deposit Account No. 13-3848 in the amount of \$ 976.00 to cover the above fees.
A duplicate copy of this sheet is enclosed.
- c. ☐ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any
overpayment to Deposit Account No. _____. A duplicate copy of this sheet is enclosed.
- d. ☐ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. **Credit card
information should not be included on this form.** Provide credit card information and authorization on PTO-2038.

**NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive 37 CFR
1.137 (a) or (b) must be filed and granted to restore the application to pending status.**

SEND ALL CORRESPONDENCE TO.

**00157**

PATENT TRADEMARK OFFICE

SIGNATURE

Diderico van Evi
NAME38,641
REGISTRATION NUMBER

PATENT APPLICATION
Mo6617
STA-155

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

APPLICATION OF)
VIKTOR STOLLER ET AL) PCT/EP00/01667
SERIAL NUMBER: TO BE ASSIGNED)
FILED: HEREWITH)
TITLE: NICKEL HYDROXIDE COATED WITH)
COBALTOUS HYDROXIDE)

PRELIMINARY AMENDMENT

Assistant Commissioner for Patents
Washington, D.C. 20231

Sir:

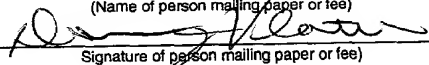
Please amend the subject patent application as follows:

"Express Mail" mailing label number ET146S94135US
Date of Deposit September 5, 2001

I hereby certify that this paper or fee is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on the date indicated above and is addressed to the Assistant Commissioner of Patents and Trademarks, Washington, D.C. 20231

Donna J. Veatch

(Name of person mailing paper or fee)


Signature of person mailing paper or fee

IN THE CLAIMS:

Please cancel Claims 1-21 and add new Claims 22-43:

--22. A coated nickel hydroxide having a cobalt(II) hydroxide coating that is stable to oxidation, wherein the nickel hydroxide has a pastel green color that does not change during storage in the atmosphere for 4 weeks.

23. A coated nickel hydroxide having a cobalt hydroxide coating that is stable to oxidation, wherein the nickel hydroxide has a content of cobalt in the 3-valent oxidation level increasing by less than 0.5%, based on the total cobalt content, after storage in air for at least 4 weeks.

24. A coated nickel hydroxide having a cobalt hydroxide coating, wherein the nickel hydroxide is stable to oxidation, and wherein the coating has 1 to 200 mmol of one or more anions of weak inorganic oxygen acids per mol of cobalt(II) hydroxide.

25. The nickel hydroxide according to Claim 24, wherein the anion is CO_3 .

26. The nickel hydroxide according to Claim 22, wherein the nickel hydroxide is in the form of powder and wherein the nickel hydroxide has an average particle size (D50 value, measured by the Mastersizer method) of 0.5 to 500 μm .

27. The nickel hydroxide according to Claim 22, wherein the nickel hydroxide is a coating on a substrate.

28. The nickel hydroxide according to Claim 22, wherein the nickel hydroxide comprises an amount of 0.2 to 25 wt.% in total of a doping element selected from the group consisting of Mg, Ca, Sr, Sc, Y, La, lanthanoids, Ti, Zr, Cr, Mo, W, Mn, Fe, Co, Cu, Zn, Cd, B, Al, Ga, In, Si, P, As, Sb and Bi, and combinations thereof.

29. The nickel hydroxide according to Claim 22, wherein the nickel hydroxide has water molecules at interstitial sites in an amount of up to 10 wt.%.

30. A process for preparing a coated nickel hydroxide having a cobalt(II) hydroxide coating that is stable to oxidation, wherein the coated nickel hydroxide has a pastel green color that does not change during storage in the atmosphere for 4 weeks,

the process comprising treating (i) optionally doped coated nickel hydroxide provided with a cobalt hydroxide coating with (ii) a weak inorganic oxygen acid selected from the group consisting of aluminate, borate, carbonate, chromate, manganate, molybdate, niobate, phosphate, silicate, tantalate, vanadate, tungstate, oxalate, alkali metal salts thereof, and mixtures thereof.

31. The process according to Claim 30, wherein the treating is carried out in an aqueous solution of alkali metal carbonate, an aqueous solution of alkali metal bicarbonate, or mixtures thereof.

32. The process according to Claim 30, wherein the process further comprises a stabilizing treatment that is carried out in an original precipitation suspension of the coating process or after prior removal of mother liquor of the original precipitation suspension and subsequent resuspending in water.

33. The process according to Claim 32, wherein the stabilizing treatment is carried out by treating an unwashed or washed filter cake directly after filtration of the mother liquor of the original precipitation suspension of the process.

34. The process according to Claim 32, wherein the stabilizing treatment is carried out by carbonation of the surface of the coated nickel hydroxide coated with cobalt(II) hydroxide.

35. The process according to Claim 34, wherein the carbonation is carried out by addition of alkali metal carbonate solutions, alkali metal bicarbonate solutions, or mixtures thereof, at concentrations of 0.01 mol/l up to the solubility maximum.

36. The process according to Claim 35, wherein the amount of alkali metal carbonate solution, alkali metal bicarbonate solution, or mixtures thereof is 0.1-10 times the weight, based on the solids content of the suspension comprising the nickel hydroxide coated with cobalt(II) hydroxide.

37. The process according to Claim 34, wherein the carbonation is carried out by addition of carbon dioxide.

38. The process according to Claim 32, wherein the stabilizing treatment is carried out at a temperature of 0-100°C.

39. The process according to Claim 30, wherein the coated nickel hydroxide coated with stabilized cobalt(II) hydroxide is washed before a final drying step.

40. The process according to Claim 30, wherein the coated nickel hydroxide coated with stabilized cobalt(II) hydroxide is dried without exclusion of air.

41. The process according to Claim 34, wherein the carbonation is carried out by treating of a moist filter cake of the nickel hydroxide coated with cobalt(II) hydroxide, in carbon dioxide or carbon dioxide-containing air under CO₂ partial pressures of 0.01 to 2 bar, optionally with simultaneous drying in continuously operated spray dryers or spin flash dryers.

42. The coated nickel hydroxide of Claim 22, wherein a doped or non-doped nickel hydroxide is coated with stabilized cobalt(II) hydroxide.

43. An electrode material in a secondary battery comprising the nickel hydroxide of Claim 42.--

IN THE SPECIFICATION:

On page 1, replace the title with the following title:

--NICKEL HYDROXIDE COATED WITH COBALTOUS HYDROXIDE--

On page 1, below the title, please add:

--This application is the National Stage Application of PCT/EP00/01667, which claims a priority from German Application 199 10 461.1, filed March 10, 1999.-

On page 1, below the line ending "March 10, 1999," add

--BACKGROUND OF THE INVENTION--

On page 3, below line 15, please add:

--DESCRIPTION--

On page 8, below line 17, please add:

--The invention is further described in the following illustrative examples in which all parts and percentages are by weight unless otherwise indicated.--

On page 11, below line 2, please add the following:

--Although the present invention has been described in detail with reference to certain preferred versions thereof, other variations are possible. Therefore, the

spirit and scope of the appended claims should not be limited to the description of the versions contained therein.--

Please add the following new Abstract, submitted herein on a separate page:

--NICKEL HYDROXIDE COATED WITH COBALT HYDROXIDE

ABSTRACT OF THE DISCLOSURE

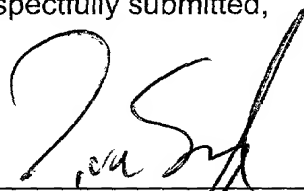
A coated nickel hydroxide for rechargeable batteries which is provided with a cobalt hydroxide coating which is stable to oxidation is described. The stability to oxidation is achieved by covering the surface of the cobalt hydroxide layer with anions of weak inorganic oxygen acids.--

REMARKS

Entry of this Preliminary Amendment is requested. The above-made amendments have been made to place the application in conformance with American standards. No new matter has been added.

Respectfully submitted,

By



Diderico van Eyl
Attorney for Applicants
Reg. No. 38,641

Bayer Corporation
100 Bayer Road
Pittsburgh, Pennsylvania 15205-9741
(412) 777-8355
FACSIMILE PHONE NUMBER:
(412) 777-8363

/jme/DVE0304

MARKED-UP VERSION SHOWING CHANGES

IN THE CLAIMS:

Claims 1-21 were cancelled and new Claims 22-43 were added:

--22. A coated nickel hydroxide having a cobalt(II) hydroxide coating that is stable to oxidation, wherein the nickel hydroxide has a pastel green color that does not change during storage in the atmosphere for 4 weeks.

23. A coated nickel hydroxide having a cobalt hydroxide coating that is stable to oxidation, wherein the nickel hydroxide has a content of cobalt in the 3-valent oxidation level increasing by less than 0.5%, based on the total cobalt content, after storage in air for at least 4 weeks.

24. A coated nickel hydroxide having a cobalt hydroxide coating, wherein the nickel hydroxide is stable to oxidation, and wherein the coating has 1 to 200 mmol of one or more anions of weak inorganic oxygen acids per mol of cobalt(II) hydroxide.

25. The nickel hydroxide according to Claim 24, wherein the anion is CO_3 .

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27. The nickel hydroxide according to Claim 22, wherein the nickel hydroxide is a coating on a substrate.

28. The nickel hydroxide according to Claim 22, wherein the nickel hydroxide comprises an amount of 0.2 to 25 wt.% in total of a doping element selected from the group consisting of Mg, Ca, Sr, Sc, Y, La, lanthanoids, Ti, Zr, Cr, Mo, W, Mn, Fe, Co, Cu, Zn, Cd, B, Al, Ga, In, Si, P, As, Sb and Bi, and combinations thereof.

29. The nickel hydroxide according to Claim 22, wherein the nickel hydroxide has water molecules at interstitial sites in an amount of up to 10 wt.%.

30. A process for preparing a coated nickel hydroxide having a cobalt(II) hydroxide coating that is stable to oxidation, wherein the coated nickel hydroxide

has a pastel green color that does not change during storage in the atmosphere for 4 weeks,

the process comprising treating (i) optionally doped coated nickel hydroxide provided with a cobalt hydroxide coating with (ii) a weak inorganic oxygen acid selected from the group consisting of aluminate, borate, carbonate, chromate, manganate, molybdate, niobate, phosphate, silicate, tantalate, vanadate, tungstate, oxalate, alkali metal salts thereof, and mixtures thereof.

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40. The process according to Claim 30, wherein the coated nickel hydroxide coated with stabilized cobalt(II) hydroxide is dried without exclusion of air.

41. The process according to Claim 34, wherein the carbonation is carried out by treating of a moist filter cake of the nickel hydroxide coated with cobalt(II) hydroxide, in carbon dioxide or carbon dioxide-containing air under CO₂ partial pressures of 0.01 to 2 bar, optionally with simultaneous drying in continuously operated spray dryers or spin flash dryers.

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43. An electrode material in a secondary battery comprising the nickel hydroxide of Claim 42.--

IN THE SPECIFICATION:

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--NICKEL HYDROXIDE COATED WITH COBALTOUS HYDROXIDE--

On page 1, below the title, the following was added:

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--BACKGROUND OF THE INVENTION--

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--DESCRIPTION--

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spirit and scope of the appended claims should not be limited to the description of the versions contained therein.--

The following new Abstract was added and submitted herein on a separate page:

--NICKEL HYDROXIDE COATED WITH COBALT HYDROXIDE
ABSTRACT OF THE DISCLOSURE

A coated nickel hydroxide for rechargeable batteries which is provided with a cobalt hydroxide coating which is stable to oxidation is described. The stability to oxidation is achieved by covering the surface of the cobalt hydroxide layer with anions of weak inorganic oxygen acids.--

NICKEL HYDROXIDE COATED WITH COBALT HYDROXIDE

ABSTRACT OF THE DISCLOSURE

A coated nickel hydroxide for rechargeable batteries which is provided with a cobalt hydroxide coating which is stable to oxidation is described. The stability to oxidation is achieved by covering the surface of the cobalt hydroxide layer with anions of weak inorganic oxygen acids.

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I hereby certify that this paper or fee is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on the date indicated above and is addressed to the Assistant Commissioner of Patents and Trademarks, Washington, D.C. 20231

Donna J. Veatch

(Name of person mailing paper or fee)

Signature of person mailing paper or fee

1/pst
Nickel hydroxide coated with cobalt hydroxide

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5 The present invention relates to a nickel hydroxide which is stable to oxidation and coated with cobalt hydroxide, and to a process for the preparation thereof, in particular for use as a positive active mass in rechargeable alkaline batteries.

10 Although nickel hydroxide is outstandingly suitable for storage of electrical energy because of its storage capacity of 1 to (with a corresponding defect structure) a theoretical maximum of 1.67 electrons per Ni, it has a number of undesirable properties, such as low electrical conductivity, low cycle stability, low charging capacity at high temperatures and the tendency to swell because of the spontaneous formation of different crystal phases with different lattice spacings.

15 In a very early stage of the development of nickel hydroxide batteries it was already recognized that the properties of the batteries can be improved by using nickel hydroxide coated with cobalt(II) hydroxide (see US-A 3 066 178). Nevertheless, the industrial use of nickel hydroxide coated with cobalt hydroxide has not since become accepted because of the sensitivity of cobalt(II) hydroxide to oxidation. Rather, the route taken in the production of the battery is the use of non-coated
20 nickel hydroxide with the addition of Co metal powder or cobalt compounds, such as Co(II)O or Co(OH)₂, where a cobalt hydroxide coating crosslinked between the nickel hydroxide particles forms on the nickel hydroxide via intermediate cobalt(II) hydroxo complexes during more prolonged standing (typically 1 to 3 days), the cobalt compound dissolving in the electrolyte, this coating then being converted into
25 the actually conductive but electrochemically inactive cobalt oxyhydroxide network during the first electrical charging of the battery. A comprehensive description of the mechanisms which are important here is to be found in the paper by Oshitani at the 3rd Symposium for Sectional New-Battery Study Group in Battery Technology Committee of the Electrochemical Society, December 11, 1986, entitled
30 "Development of high-capacity nickel-cadmium battery using sintered metal fiber as

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substrate". The models described there in respect of cobalt compounds also apply to other substrates and cathode materials.

When nickel hydroxides which are coated according to the prior art with a cobalt(II) hydroxide layer which is not stable to oxidation by atmospheric oxygen are used, in the course from production via storage to the actual use in the battery a passivating cobalt(II)-containing layer forms on the surface of the coated nickel hydroxide particles, this not only impeding the solubility of the cobalt species to give the cobalt hydroxo complexes to be formed intermediately (reduction in the contact surface due to inadequate fusion), but additionally having a poor electrical conductivity. This then necessarily means that large parts of the active nickel mass are not accessible electrically and as more or less dead material can no longer contribute towards the capacity of the battery.

It has also already been proposed (Japanese Patent 25 89 123) to generate the conductive electrochemically inactive cobalt oxyhydroxide layer by precipitating a cobalt hydroxide layer on to the nickel hydroxide particles and subsequently oxidizing the layer in alkaline solution by means of oxygen at a higher temperature. Such nickel hydroxide coated with cobalt oxyhydroxide is indeed stable to oxidation; however, a disadvantage is the fact that although the individual particles in its outer shell have a good conductive layer, the formation of a three-dimensional conductive network between the individual particles (increasing the contact surface by "fusion") can be achieved only by further addition of cobalt compounds which are adequately soluble in the alkaline electrolyte. If this addition is omitted, only loose contact points exist between the individual particles and the total resistance of the electrode is increased because of the transition resistance which occurs between the individual particles.

On the other hand, a cobalt(II) hydroxide coating remains soluble in the alkaline electrolyte to the extent that crosslinking takes place by dynamic dissolving and addition processes, so that conductivity bridges are generated between the particles after conversion to cobalt oxyhydroxide during the initialization charging cycle. The

coated individual particles are "fused" in an electrically conductive manner at the contact points of the $\text{Co}(\text{OH})_2$ or CoOOH coating. A condition of this, however, is the provision of a nickel hydroxide with a cobalt(II) hydroxide coating which is stable to oxidation.

5

Accordingly, it has also already been proposed to treat cobalt(II) hydroxide (as a conductive additive to nickel hydroxide) or nickel hydroxide coated with cobalt(II) hydroxide with antioxidants, such as D-glucose (EP-A 744 781) or higher carboxylic acids, their esters, aldehydes, phenols or vitamins (EP-A 771 041). A disadvantage here is that the protection against oxidation is achieved only indirectly, since the antioxidants only become active with respect to the oxidized cobalt(II) form in the sense of a reduction. A further disadvantage is that the antioxidant is consumed in the course of time, that is to say the oxidation protection is limited with respect to time. There is furthermore the risk that undesirable degradation products of the antioxidant are entrained into the battery.

15

It has now been found that the cobalt hydroxide layer can be formed in a form which is stable to oxidation if the coated nickel hydroxide is treated with weak inorganic oxygen acids or alkali metal salts thereof. In this procedure, the surface of the coated particles is covered with anions of the acids. Suitable anions are one or more anions from the group consisting of aluminate, borate, carbonate, chromate, manganate, molybdate, niobate, phosphate, silicate, tantalate, titanate, vanadate and tungstate, or oxalates.

20

Borate, phosphate, carbonate and/or silicate are preferred. Carbonate is particularly preferred.

25

"Stable to oxidization" in the context of the invention means that the degree of oxidation of the cobalt hydroxide does not change during storage in air and at ambient temperature (up to 40°C).

30

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Li, Na, K and/or pseudo-alkali metals, such as ammonium, are suitable as the alkali metal. The treatment is preferably carried out in an aqueous solution of the alkali metal salts, in particular of the sodium salt.

- 5 A less than monomolecular covering of the Co(OH)_2 surface is sufficient to render the nickel hydroxide provided with the Co(OH)_2 coating stable to oxidation.

10 It has been found that such a surface covering does not impair the solubility of the cobalt(II) hydroxide coating in the alkaline electrolyte of the battery, so that the effect of the formation of a three-dimensional network of high conductivity, called "fusion" above, can also take place unimpeded without the addition of a further conductive additive. As a result, it is possible to keep the total amount of cobalt employed to a minimum.

- 15 The invention provides a nickel hydroxide which is provided with a cobalt hydroxide layer which is stable to oxidation and the pastel green colour of which is retained during storage in the atmosphere for a period of at least 4 weeks; preferably for a period of 6 months.

- 20 The invention also provides a nickel hydroxide provided with a cobalt hydroxide layer which is stable to oxidation, the content of cobalt in the 3-valent oxidation level increasing by less than 0.5%, based on the total content of cobalt, even after storage in air (ambient temperature 10 to 35°C) for at least 6 months.

- 25 The oxidation level of the cobalt here is preferably determined by iodometric titration in a manner known per se.

30 The invention furthermore provides a nickel hydroxide which is provided with a cobalt hydroxide coating and has on its surface an at most monomolecular layer of anions of weak inorganic oxygen acids. The concentration of the anion of the weak acid is preferably 5 to 20 $\mu\text{mol/m}^2$ of surface coated with cobalt hydroxide. A surface covering of 10 to 18 $\mu\text{mol/m}^2$ is especially preferred.

The superficial anion concentration is preferably 10 to 50 mmol per mol of cobalt(II) hydroxide, based on the amount of the cobalt hydroxide coating.

- 5 The nickel hydroxide powder according to the invention is preferably free from antioxidants or organic degradation products thereof.

Fig. 1 explains the invention by comparison with the prior art.

- 10 The circles A represent diagrams of a nickel hydroxide particle, the grey structure B represents a Co(OH)_2 coating, the broken circle C represents a partial oxidation of the Co(OH)_2 coating and the dark structure D represents a CoOOH coating.

- 15 Fig. 1a) explains the prior art, according to which a nickel hydroxide (I) coated with Co(OH)_2 which is not stable to oxidation is partly oxidized (II) on the surface by contact with ambient air. As a result, the hydroxo complex formation in the electrolyte (III) is impeded. Even after forming, only a partial conductivity network can thereby form (IV).

- 20 Fig. 1b) explains the generation of a CoOOH coating by conversion of the Co(OH)_2 coating by alkaline oxidation at elevated temperature (I). The conductivity of the active mass in the battery is determined by loose point contacts (IV).

- 25 Fig. 1c) shows the nickel hydroxide (I, II) which is provided according to the invention with a Co(OH)_2 coating which is stable to oxidation, and which remains soluble (III) in the electrolyte via hydroxo complexes and therefore forms a Co(OOH) network on forming (first charging and discharging cycles).

- 30 The nickel hydroxide to be employed according to the invention can be prepared in any desired manner.

Known processes for the preparation of nickel hydroxide are chemical precipitation from aqueous nickel salt solutions by means of alkali metal hydroxide solutions,

electrolytic dissolving of nickel anodes in an aqueous salt-containing electrolyte, oxidation of nickel metal powder under pressure, dissolving of nickel powder as a complex in an ammonia solution and subsequent precipitation by distillation, and by oxidizing hydrolysis and subsequent reduction of alkali metal nickelates. Processes of chemical precipitation or of electrolytic dissolving of nickel anodes are preferred. A spherical nickel hydroxide which is prepared by one of the known processes of the prior art is preferably employed.

The nickel hydroxide base particles prepared by one of the known processes are first coated with cobalt(II) hydroxide in a first step in aqueous suspension with the addition of cobalt(II) salts and alkali metal hydroxide solution and/or ammonia under suitable conditions. Preferred conditions for achieving a uniform cobalt(II) hydroxide coating are: continuous, semi-batch or batch process procedure, residence time 0.2 to 12 h; temperature 0 to 120°C, preferably 30 to 60°C, and particularly preferably 30 to 40°C; pressure 0.1 to 2.5 bar, preferably 0.5 to 1.2 bar; pH at 25°C 8.5 to 13, preferably 9.5 to 11.5, and particularly preferably 10.2 to 10.8; solids concentration 10 to 700 g/l, preferably 100 to 400 g/l; NH₃ content 0 to 15 g/l, preferably 0 to 10 g/l, particularly preferably 2 to 5 g/l; alkali metal/cobalt ratio 75 to 150%, preferably 80 to 95% of the stoichiometry; optionally filtration, washing with water and/or dilute alkali metal hydroxide solution, preferably sodium hydroxide solution with a pH of 11 to 12. The coating with cobalt(II) hydroxide can also be carried out without an inert gas or the addition of antioxidants.

To stabilize the cobalt(II) hydroxide coating by rendering the surface inert, the original precipitation suspension of the coating process or, preferably, the nickel hydroxide which has been coated with cobalt(II) hydroxide and has already been separated off from the mother liquor and resuspended in water is then treated in a second step with the weak acids listed above or aqueous alkali metal salts or alkali metal hydrogen salts thereof. The stabilizing treatment can also be carried out directly after filtration of the mother liquor of the original precipitation suspension of the coating process, by treatment of the unwashed or washed filter cake. The temperature range of the stabilizing treatment is 0 to 100°C, preferably 20 to 60°C,

and particularly preferably 40 to 50°C. The duration of the treatment can be 0.2 to 12 hours.

5 It has proved to be particularly advantageous to carry out the stabilizing treatment by carbonation of the surface of the nickel hydroxide coated with cobalt(II) hydroxide. The carbonation here is preferably carried out by addition of alkali metal carbonate and/or alkali metal bicarbonate solutions at concentrations from 0.01 mol/l up to the solubility maximum, preferably 0.03 to 1 mol/l, the amount of alkali metal carbonate and/or alkali metal bicarbonate solution being 0.1 to 10 times the weight, based on
10 the solids content of the suspension which comprises the nickel hydroxide coated with cobalt(II) hydroxide. In the context of the invention, the carbonation then also proceeds if the carbonation takes place by addition of carbon dioxide, e.g. introduction as a gas.

15 A particularly preferred embodiment of the invention comprises treating the still moist filter cake from the cobalt hydroxide coating or the subsequent washing in carbon dioxide or carbon dioxide-containing air under CO₂ partial pressures of 0.01 to 2 bar, preferably 0.01 to 1 bar. The treatment can be carried out simultaneously with the drying of the powders, for example in continuously operated spray dryers or
20 spin flash dryers.

The nickel hydroxide coated with a stabilized cobalt(II) hydroxide layer after the stabilizing treatment has been concluded can optionally also additionally be washed before the final drying step. The drying itself does not have to be carried out with
25 exclusion of air (vacuum or inert gas), but drying can be carried out in air to save costs. All the conventional types of dryer can be used as drying units.

Although pulverulent nickel hydroxide is preferred according to the invention, the invention is not limited to pulverulent nickel hydroxide. According to the invention,
30 it is possible in an analogous manner first to precipitate nickel hydroxide on to a substrate, preferably a nickel gauze, nickel nonwoven or a nickel foil, subsequently

to coat this with cobalt hydroxide and then to immerse the coated substrate into the treatment solution.

5 Preferred base nickel hydroxides have average particle sizes (D50 value, measured by the Mastersizer method) of 0.5 to 500 μm , particularly preferably 2 to 30 μm . The specific surface area can advantageously be 2 to 70 m^2/g , measured by the BET method.

10 The base nickel hydroxide can furthermore comprise one or more doping elements known per se from the group consisting of magnesium, calcium, strontium, scandium, yttrium, lanthanum, lanthanoids, titanium, zirconium, chromium, molybdenum, tungsten, manganese, iron, cobalt, copper, cadmium, zinc, boron, aluminium, gallium, indium, silicon, phosphorus, arsenic, antimony and bismuth, in amounts of 0.2 to 25 wt.% in total. Preferred nickel hydroxides are doped with 0.5
15 to 5 wt.% zinc and 0.5 to 5 wt.% cobalt in a total amount of 3 to 8 wt.%.

The cobalt hydroxide coating can also comprise doping elements from the abovementioned group in a manner known per se.

The invention is illustrated in more detail by the following example:

Example

5 348.5 g/h of a CoCl_2 solution (7.0% Co), 297.5 g/h of a 10% NaOH solution, 180 ml/h of a 100 g/l NH_3 solution and 3,000 ml/h of an $\text{Ni}(\text{OH})_2$ suspension (150 g/l of spherical $\text{Ni}(\text{OH})_2$ doped with Co and Zn, 80 g/l NaCl, 3.5 g/l Na_2SO_4) are continuously metered in parallel into a 17 litre stirred reactor temperature-
10 controlled at 37°C. A pH (25°C) of 10.5 and an NH_3 content (Kjeldahl) of approx. 3.5 g/l are established here in the equilibrium state. After a first runnings time of 24 hours, the outflow from the reactor (approx. 3,750 ml/h) is collected at 24 h intervals for a further 72 hours, filtered batchwise and washed with in each case 23 kg of temperature-controlled 0.2 g/l NaOH solution (45°C). The residue on the filter is
15 then treated with 46 kg 1.0 mol/l Na_2CO_3 solution (45°C) and finally washed with 46 kg completely demineralized water (45°C). Drying is carried out at 50°C in vacuo. The product yield is 11.7 kg per 24 h batch.

20 Table 1 shows analytical values of the non-coated base nickel hydroxide. Table 2 shows analytical values of the nickel hydroxide coated with cobalt hydroxide with oxidation-stabilizing treatment immediately after preparation and after storage in air for 6 months.

Table 1

Ni(OH) ₂ base material, non-coated							
Ni	Co _{tot.}	Co(III)	Zn	Cl	Na	SO ₄	C
(%)	(%)	(%)	(%)	(ppm)	(ppm)	(ppm)	(ppm)
57.17	1.44	0.5	3.65	360	31	80	1,100
TD	MS	CS	BET				
(g/cm ³)	D ₅₀ (μm)	(Å)	(m ² /g)				
2.0	4.5	70	19.84				

Table 2

Ni(OH) ₂ base material according to the invention, coated with Co(OH) ₂ and CO ₃							
Ni	Co _{tot.}	Co(III)	Zn	Cl	Na	SO ₄	C
(%)	(%)	(%)	(%)	(ppm)	(ppm)	(ppm)	(ppm)
52.92	6.44	0.7	3.36	420	35	140	1,400
TD	MS	CS	BET		Co(III) after storage in air for 6 months		
(g/cm ³)	D ₅₀ (μm)	(Å)	(m ² /g)		(%)		
2.0	5.11	70	17.42		0.7		

TD = tap density; MS = particle size determined by the Mastersizer method;

CS = crystallite size determined by X-ray analysis;

5 BET = specific surface area measured by the BET method, % values = wt.%.

The nickel hydroxide material coated according to the invention and prepared according to the example is measured, after storage in air for 6 months, in the half cell test without any addition of a conductive additive in the electrode production and, from the 3rd (charging and discharging) cycle, reaches 99% of the Ni utilization, based on the one-electron step.

A conventional three-electrode arrangement which comprises an Hg/HgO reference electrode, a nickel plate counter-electrode and the working electrode comprising the nickel hydroxide active mass is chosen here. The electrochemical measurement takes place galvanostatically, i.e. a constant charging and discharging current is set between the working electrode and counter-electrode. The potential of the working electrode against the potential of the reference electrode is measured. The cyclic operation is effected by 15 hours of charging with I₁₀ (I₁₀ designates the charging current which delivers 100% of the theoretical charging capacity in 10 hours) and discharging with I₁₀ to 0 V vs. Hg/HgO. An aqueous potassium hydroxide solution is used as the electrolyte. To prepare the working electrode, the nickel hydroxide

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material according to the invention is prepared as a foam electrode and then measured.

Patent claims

1. Nickel hydroxide comprising a cobalt(II) hydroxide coating which is stable to oxidation, the pastel green colour of which does not change during storage in the atmosphere for 4 weeks.
2. Nickel hydroxide comprising a cobalt hydroxide coating which is stable to oxidation, the content of cobalt in the 3-valent oxidation level increasing by less than 0.5%, based on the total cobalt content, after storage in air for at least 4 weeks.
3. Nickel hydroxide with a cobalt hydroxide coating which is stable to oxidation, the coating comprising 1 to 200 mmol of one or more anions of weak inorganic oxygen acids per mol of cobalt(II) hydroxide.
4. Nickel hydroxide according to claim 3, wherein the anion is CO_3 .
5. Nickel hydroxide according to one of claims 1 to 4 in the form of powder with an average particle size (D50 value, measured by the Mastersizer method) of 0.5 to 500 μm .
6. Nickel hydroxide according to one of claims 1 to 5 in the form of the coating on a substrate.
7. Nickel hydroxide according to one of claims 1 to 6, comprising one or more doping elements from the group consisting of Mg, Ca, Sr, Sc, Y, La, lanthanoids, Ti, Zr, Cr, Mo, W, Mn, Fe, Co, Cu, Zn, Cd, B, Al, Ga, In, Si, P, As, Sb and Bi in amounts of 0.2 to 25 wt.% in total.
8. Nickel hydroxide according to one of claims 1 to 7, comprising water molecules at interstitial sites in an amount of up to 10 wt.%.

9. Process for the preparation of nickel hydroxide according to one of claims 1 to 8, characterized in that optionally doped nickel hydroxide provided with a cobalt hydroxide coating is treated with a weak inorganic oxygen acid from the group consisting of aluminate, borate, carbonate, chromate, manganate, molybdate, niobate, phosphate, silicate, tantalate, vanadate and tungstate or oxalate or alkali metal salts thereof.
10. Process according to claim 9, characterized in that the treatment is carried out in an aqueous solution of alkali metal carbonate and/or alkali metal bicarbonate.
11. Process according to one of claims 9 to 10, characterized in that the stabilizing treatment is carried out in the original precipitation suspension of the coating process or after prior removal of the mother liquor of the original precipitation suspension and subsequent resuspending in water.
12. Process according to one of claims 9 and 11, characterized in that the stabilizing treatment is carried out directly after filtration of the mother liquor of the original precipitation suspension of the coating process, by treatment of the unwashed or washed filter cake.
13. Process according to one of claims 9 to 12, characterized in that the stabilizing treatment is carried out by carbonation of the surface of the nickel hydroxide coated with cobalt(II) hydroxide.
14. Process according to claim 13, characterized in that the carbonation is carried out by addition of alkali metal carbonate and/or alkali metal bicarbonate solutions at concentrations of 0.01 mol/l up to the solubility maximum, preferably 0.03 - 0.1 mol/l.
15. Process according to claim 14, characterized in that the amount of alkali metal carbonate solution and/or alkali metal bicarbonate solution is 0.1-10

times the weight, based on the solids content of the suspension comprising the nickel hydroxide coated with cobalt(II) hydroxide.

- 5 16. Process according to claim 13, characterized in that the carbonation is carried out by addition of carbon dioxide.
- 10 17. Process according to one of claims 9 to 16, characterized in that the stabilizing treatment is carried out at a temperature of 0-100°C, preferably 20-60°C, and particularly preferably 40-50°C.
- 15 18. Process according to one of claims 9 to 17, characterized in that the nickel hydroxide coated with stabilized cobalt(II) hydroxide is washed before the final drying step.
- 20 19. Process according to one of claims 9 to 18, characterized in that drying of the nickel hydroxide coated with stabilized cobalt(II) hydroxide is carried out without exclusion of air.
- 25 20. Process according to claim 13, characterized in that the carbonation is carried out by treatment of the moist filter cake, comprising the nickel hydroxide coated with cobalt(II) hydroxide, in carbon dioxide or carbon dioxide-containing air under CO₂ partial pressures of 0.01 to 2 bar, preferably 0.01 to 0.1 bar, preferably with simultaneous drying in continuously operated spray dryers or spin flash dryers.
21. Use of the doped or non-doped nickel hydroxide coated with stabilized cobalt(II) hydroxide, according to one of claims 1 to 20, as an electrode material in secondary batteries.

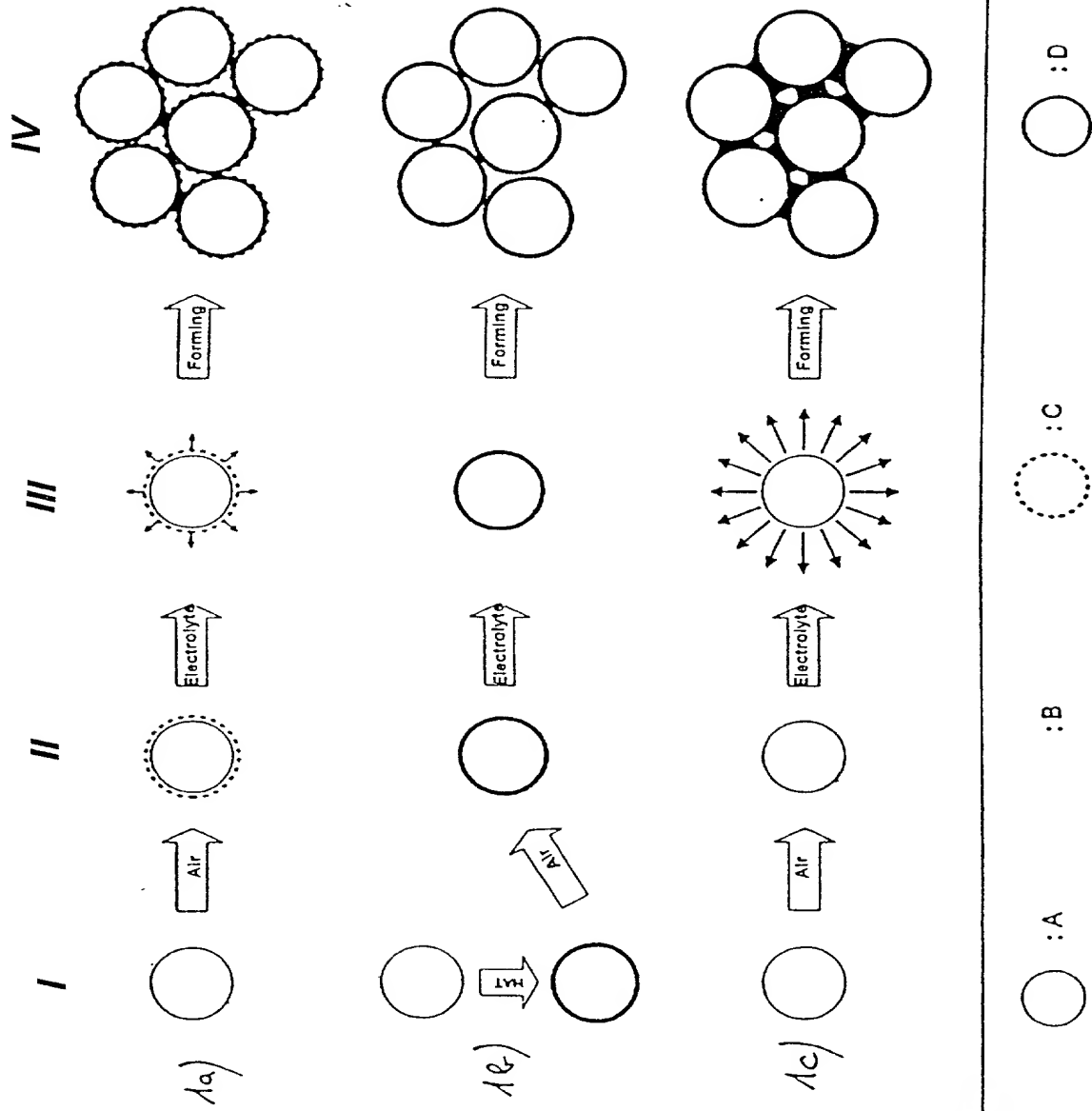


FIGURE 1

COMBINED DECLARATION AND POWER OF ATTORNEY

ATTORNEY DOCKET NO

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name. I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought

on the invention entitled

NICKEL HYDROXIDE COATED WITH COBALTOUS HYDROXIDE

the specification of which is attached hereto,

or was filed on **February 28, 2000**

as a PCT Application Serial No. **PCT/EP00/01667**

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims.

I acknowledge the duty to disclose information which is material to the patentability of this application in accordance with Title 37, Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s), the priority(ies) of which is/are to be claimed:

199 10 461.1
(Number)

Germany
(Country)

March 10, 1999
(Month/Day/Year Filed)

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose the material information as defined in Title 37, Code of Federal Regulations, §1.56 which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

(Application Serial No.)

(Filing Date)

(Status)

(patented, pending, abandoned)

(Application Serial No.)

(Filing Date)

(Status)

(patented, pending, abandoned)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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HC

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and this application and to transact all business in the Patent and Trademark Office conne

JOSEPH C. GIL, Patent Office Registration Number 26,602 ARON PREIS, Patent Office Registration Number 29,426
LYNDANNE M. WHALEN, Patent Office Registration Number 29,457 THOMAS W. ROY,
Patent Office Registration Number 29,582 RICHARD E. L. HENDERSON, Patent Office Registration Number 31,619
GODFRIED R. AKORLI, Patent Office Registration Number 28,779 N. DENISE BROWN, Patent Office
Registration Number 36,097 NOLAND J. CHEUNG, Patent Office Registration Number 39,138
DIDERICO VAN EYL, Patent Office Registration Number 38,641 CAROLYN M. SLOANE, Patent Office
Registration Number 44,339 JAMES R. FRANKS, Patent Office Registration Number 42,552
JACKIE ANN ZURCHER, Patent Office Registration Number 42,251
RAYMOND J. HARMUTH, Patent Office Registration Number 33,896

all of Bayer Corporation, Pittsburgh, Pennsylvania 15205-9741

Send Correspondence To: Direct Telephone Calls To:
Patent Department
Bayer Corporation (412) 777-2349
100 Bayer Road
Pittsburgh, Pennsylvania 15205-9741

FULL NAME OF SOLE OR FIRST INVENTOR Viktor Stoller		INVENTOR'S SIGNATURE <i>Viktor Stoller</i>	DATE 17.09.2001
RESIDENCE D 38667 Bad Harzburg, Germany DEX		CITIZENSHIP German	
POST OFFICE ADDRESS Am Wildpark 17, D 38667 Bad Harzburg, Germany			
FULL NAME OF SECOND INVENTOR Michael Erb		INVENTOR'S SIGNATURE <i>Michael Erb</i>	DATE 17.9.2001
RESIDENCE D 38259 Salzgitter, Germany DEX		CITIZENSHIP German	
POST OFFICE ADDRESS Gittertor 55, D 38259 Salzgitter, Germany			
FULL NAME OF THIRD INVENTOR Armin Olbrich		INVENTOR'S SIGNATURE <i>Armin Olbrich</i>	DATE 8/27/01
RESIDENCE D 38723 Seesen, Germany DEX		CITIZENSHIP German	
POST OFFICE ADDRESS Alte Dorfstr. 20, D 38723 Seesen, Germany			
FULL NAME OF FOURTH INVENTOR Juliane Meese-Marktscheffel		INVENTOR'S SIGNATURE <i>Juliane Meese-Marktscheffel</i>	DATE 6.9.2001
RESIDENCE D 38640 Goslar, Germany DEX		CITIZENSHIP German	
POST OFFICE ADDRESS Nußanger 8, D 38640 Goslar, Germany			
FULL NAME OF FIFTH INVENTOR		INVENTOR'S SIGNATURE	DATE
RESIDENCE		CITIZENSHIP	
POST OFFICE ADDRESS			
FULL NAME OF SIXTH INVENTOR		INVENTOR'S SIGNATURE	DATE
RESIDENCE		CITIZENSHIP	
POST OFFICE ADDRESS			
FULL NAME OF SEVENTH INVENTOR		INVENTOR'S SIGNATURE	DATE
RESIDENCE		CITIZENSHIP	
POST OFFICE ADDRESS			